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Pseudocapacitance of α -CoMoO₄ nanoflakes in non-aqueous electrolyte and its bi-functional electrocatalytic activity for methanol oxidation

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A b s t r a c t

Nanocrystalline cobalt molybdate (CoMoO₄) nanoflakes were grown directly on carbon fibre cloth (CFC) via a simple hydrothermal method without any template or surfactant. A symmetric supercapacitor was fabricated using CoMoO₄ nanoflakes/CFC as both negative and positive electrodes. The device has delivered the maximum specific capacitance of 8.3 F g⁻¹ at a constant current density of 1 A g⁻¹ in organic electrolyte. It offers the reasonable energy (2.6 Wh kg⁻¹) and power density (748.8 W kg⁻¹) as comparable to the carbon based symmetric supercapacitors. As a catalyst for methanol oxidation, the CoMoO₄ nanoflakes showed high current density (25 mA cm⁻²) and low onset potential (0.38 V). The impressive bi-functional electrochemical activity of CoMoO₄ on CFC is mainly attributed to its porous microstructure, where reasonable electrical conductivity resulted from binder-free and intimate metal oxide/substrate integration.

Introduction

Ever increasing energy demand and limited availability of fossil fuels coupled with high prices and environmental issues in today's globalized world are driving the search for sustainable energy storage and conversion devices [1e4]. Nevertheless, direct methanol fuel cells (DMFCs) and supercapacitors (SCs) are the most promising devices in the field of energy conversion and storage, which becomes highly desirable for various technological applications [3,5e8]. One of

the most encouraging applications is their use in low-emission hybrid electric vehicles and fuel cell vehicles. In such cases, supercapacitors are coupled with fuel cells to serve as a temporary energy storage device with a high-power capability to store energies when braking [9]. Therefore, supercapacitors are likely to show equal importance to batteries and fuel cells for future energy storage systems. Similarly, the development of new catalysts (non-noble) to increase the electroactivity related to methanol oxidation is important for DMFCs [10]. It is well accepted that electrode/catalyst materials are the major component to determine

device performance, thereby they have received great attention in recent years [2,4,11e16]. In particular, non-precious and low cost transition metal oxide-based electrodes and catalysts are desirable, because they are electrochemically more active and exhibit good tolerance to surface poisoning by methanol oxidation. Therefore, recent work has been focused on the use of non-precious transition metal oxides such as NiO [17e19], MnO₂ [20e22], Co₃O₄ [23e27] and CuO [28e30] based electrode and catalyst materials for SCs as well as DMFCs. Specifically, the porous transition metal oxides are of special interest to the research community for potential applications in supercapacitors, lithium batteries and fuel cells [26]. From the earlier investigations mentioned above it is understood that the electrochemically active transition metal oxides are the most important candidates for future energy conversion/storage devices. It is also very interesting to find a material with bi-functionality (to be used in both fuel cells and supercapacitors) and enhanced electrochemical activity compared to other state of art the materials.

In recent years, metal molybdates have received considerable attention for energy storage applications in particular for supercapacitors. Among them transition metal (TM) molybdates with ABO₄ (A ¼ TM, B ¼ Mo) structure inclusive of NiMoO₄, CoMoO₄, MnMoO₄ and their hybrids have been demonstrated as the superior electrode materials for supercapacitors [31e42]. There are limited reports showing complete cell performance of these materials and in particular for non-aqueous electrolytes. Also, the methanol electro-oxidation of metal molybdates have not yet been investigated. It's widely accepted that the direct integration of metal oxide nanostructures on conducting substrates can meet the practical requirements of the supercapacitor and fuel cell devices. Wei Hong et al. has constructed the Co₃O₄@NiMoO₄ hybrid nanostructure and investigated it as an asymmetric supercapacitor. Similarly, NiCo₂O₄ nanostructures on a conducting substrate have been reported for methanol electro-oxidation by Lei Qian et al. [43]. Recently, carbon fiber cloth (CFC) has been demonstrated as an ideal flexible substrate and binder-free electrode for supercapacitors [31e33,39,40]. Unlike common metallic substrates, CFC can facilitate rapid ion/electron transport in addition to its useful characteristics for SC and DMFC applications, e.g., high conductivity (<20 mU cm), chemical stability, flexibility, and three-dimensional structures [39,42]. To date, various methods have been developed to design electrode materials onto highly flexible CFC. However, tedious and complicated synthesis processes were adopted to obtain a well-integrated 3D hierarchical architecture on flexible substrate with desired morphology. Especially for metal molybdate based electrode on CFC, only limited reports are available [35]. Recently, Di Guo et al. reported NiMoO₄ nanowires on CFC as the advanced electrode for symmetric supercapacitors [35]. Among the metal molybdates, CoMoO₄ exhibits impressive electrochemical response in both alkaline and neutral electrolytes. However, their inadequate phase in low temperature, limits their large scale applications. Therefore, it will be of great significance to develop a synthesis of CoMoO₄ nanostructure on a flexible substrate with desired phase and morphology.

Herein, we report a simple hydrothermal approach to design hierarchical a-CoMoO₄ nanoflakes on carbon fiber

cloth. The electrochemical characteristic of the material has been investigated as a binder free electrode for a supercapacitor in nonaqueous electrolyte and an electrocatalyst for methanol oxidation in an alkaline medium. As an electrode for a symmetric supercapacitor, the material exhibits a maximum specific capacitance of 8.3 F g⁻¹ at a constant current density of 1 A g⁻¹ and long term cyclic stability (10,000 cycles) in 1 M Tetraethyl Ammonium Tetra Fluoroborate (TEABF₄) in Propylene Carbonate (PC). Interestingly, the a-CoMoO₄/CFC nanoflakes structure showed excellent electrocatalytic activity towards methanol oxidation with a high current density (25 mA cm⁻²) and lowest onset potential (0.38 V) compared to other transition metal oxide catalysts.

Experimental techniques

Fabrication

The synthesis of a-CoMoO₄ nanoflakes on CFC is described as follows: CFC (4 x 4 cm²), was treated with 3 M HCl for 15 min, followed by washing with ethanol and deionized water and then used as a substrate. To integrate CoMoO₄ on CFC, 0.1 M of Co(NO₃)₂·6H₂O and 0.1 M Na₂MoO₄·2H₂O were dissolved in equal volume (1:1) of water and ethanol mixed solvents separately under stirring. Molybdate ions containing solution were added drop-wise to the cobalt ion solution and stirred continuously for 30 min. A violet-colored precipitated suspension of 100 ml volume was transferred to the autoclave, which contained the pre-treated CFC substrate and was kept at 180 °C for 12 h in the oven. After that, the autoclave was left to cool to room temperature. Finally, CFC was washed with DI water and calcined for 2 h at 500 °C under Ar atmosphere. The amount of CoMoO₄ was measured from the weight difference of the pure CFC and CoMoO₄ grown CFC. The typical mass of the active electrode material is ~0.5 mg cm⁻².

Characterization

The crystalline structure of the CoMoO₄ sample was evaluated by X-ray diffraction (Philips X'Pert Pro; Cu Ka, λ ¼ 0.1542 nm). The Raman scattering spectra of CoMoO₄/CFC were recorded using Renishaw InVia Raman spectrometer using a 514 nm 30 mW Argon Ion laser, where spectra were collected using a RenCam CCD camera. The beam was focused onto the samples using either a 20 x /50 x objective lens. The morphology and microstructure of CFC-supported CoMoO₄ electrode was characterized using high resolution scanning electron microscope (HRSEM) (FEI QUANTA 200F HRSEM), and a high resolution transmission electron microscope (HRTEM) (TECNAI HRTEM-3010 at 200 kV). The capacitive performance of the samples was evaluated on a CHI 660C electrochemical workstation using cyclic voltammetry (CV), chronopotentiometry (CP), and electrochemical impedance spectroscopy (EIS) techniques. The symmetric supercapacitor was fabricated by using CoMoO₄/CFC as a binder-free working electrode. 1 M TEABF₄ in propylene carbonate (PC) solution was used as the supporting electrolyte. For fuel cell application, the electrocatalytic activity of the electrode was studied in 1 M KOH solution with and without 0.5 M CH₃OH by cyclic voltammetry,

chronoamperometry and electrochemical impedance spectroscopy (EIS). A Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes for this study.

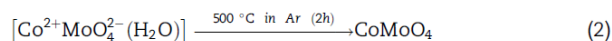
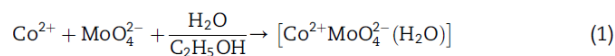
Results and discussion

Structure analysis

The crystal structure of the CoMoO_4 grown on CFC was investigated by XRD analysis. Fig. 1(a) shows the XRD pattern of CoMoO_4 nanoflakes and the inset represents the XRD pattern of pure CFC. The broad peak with splitting at $\sim 26.10^\circ$ can be assigned to the (002) plane of $\alpha\text{-CoMoO}_4$ as well as the reflection of CFC [41]. Similarly, the diffraction peaks positioned at 27.4° , 31.2° , 34.1° , 37.08° , 39° , 42.6° and 47.1° can be indexed to the (-112), (131), (-222), (040), (003), (132) and (-511) planes of $\alpha\text{-CoMoO}_4$. The observed broad diffraction peaks can be ascribed to the formation of nanocrystalline $\alpha\text{-CoMoO}_4$ which is well-matched to the corresponding JCPDS file (210868) [31,44]. In order to avoid the confusion of crystalline structure, the XRD analysis of the powder sample collected from the remaining precipitate formed during the hydrothermal process was carried out and is shown in Fig. S1. It further supports the formation of $\alpha\text{-CoMoO}_4$ nanocrystalline. Raman scattering analysis further confirmed the formation of CoMoO_4 on carbon fibre cloth. Fig. 1(b) shows the Raman spectra of CoMoO_4 nanoflakes on CFC and the inset represents the Raman bands of pure CFC. The observed Raman bands for CoMoO_4 are 333, 363, 697, 808, 884 and 928 cm^{-1} . The bands at 884 and 928 cm^{-1} and the low wavenumber band at 333 cm^{-1} are related to the Mo-Oe-Co stretching vibrations in CoMoO_4 [44,45]. The Co-O vibrational band was observed at 528 cm^{-1} [45]. The band at 697 cm^{-1} further confirms the formation of $\alpha\text{-CoMoO}_4$, which is in good agreement with XRD results [46]. As with pure CFC, the high intensity D band (disordered carbon) and G band (graphitic carbon) of carbon are found with Raman shifts of ~ 1353 and 1581 cm^{-1} , respectively (see inset of Fig. 1(b)) [47].

The surface morphology of CoMoO_4 directly grown on CFC was examined by SEM and TEM. Fig. 2(a-d) shows the SEM images of CoMoO_4 on CFC. The low magnification SEM images as shown in Fig. 2(a and b) showed the growth of well-

integrated nanoflakes over the CFC surface in a uniform manner. The CoMoO_4 completely covered the CFC with interconnected nanoflakes. The high magnification SEM images of Fig. 2(d) clearly shows that the nanoflakes are composed of fine nanocrystals and exhibit an open network of porous microstructure. It should be noted that this interesting microstructure can provide large volume space to accommodate electrolyte ions and increase active sites to the redox process. The composition of the elements present in CoMoO_4 nanoflakes are confirmed with energy dispersive X-ray spectrum (EDS) analysis, which is shown in Fig. S2 (ESI). The EDS shows the dominant carbon peak from the substrate in addition to the primary Co, Mo and O elements in appropriate concentrations. This result confirms the phase purity of the compound. Typical TEM images of Fig. 3(a) and (b) indicate the nanocrystals of 7 ± 12 nm randomly oriented, and form the interconnected nanoflake microstructure. From high magnification TEM images of Fig. 3(c), the characteristic porous microstructures of CoMoO_4 nanoflakes are visible. The selected area electron diffraction pattern (SAED) shown in Fig. 3(d) confirms the polycrystalline growth of $\alpha\text{-CoMoO}_4$ over the CFC. The selected rings are well matched to the corresponding $\{hkl\}$ planes of standard CoMoO_4 nanocrystals. Based on this observation, the growth of CoMoO_4 nanoflakes can be described by the following chemical reactions [48]:



Initially, hydrated cobalt molybdate complex was

formed, which may interact electrostatically with the CFC. Under hydrothermal conditions, nucleation of CoMoO_4 occurred, followed by the growth of CoMoO_4 nanoflakes on the CFC surface.

Symmetric supercapacitor

The electrochemical characteristic of the CoMoO_4 nanoflakes electrodes was investigated as a symmetric supercapacitor in 1 M TEABF₄ in PC electrolyte by cyclic voltammetry, charge-discharge and electrochemical impedance measurements. Typical electrochemical responses of $\text{CoMoO}_4/\text{CFC}$ are shown in Fig. 4(a-d). Cyclic voltammograms of

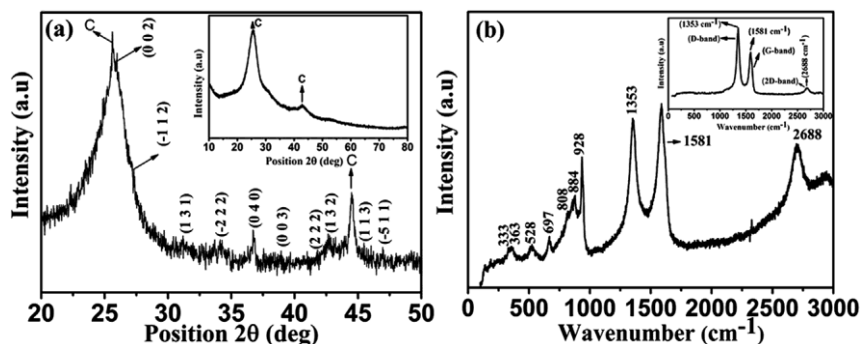


Fig. 1 (a) XRD pattern and (b) Raman spectrum of $\text{CoMoO}_4/\text{CFC}$ and pristine CFC.

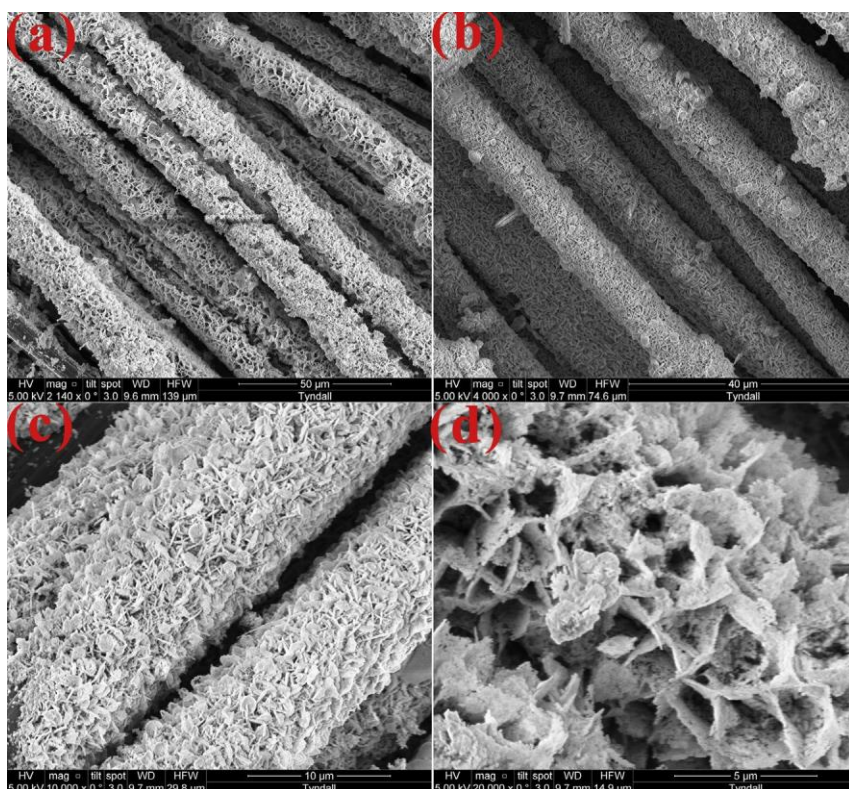


Fig. 2 (a-d) HRSEM images of CoMoO₄ nanoflakes structure on CFC.

CoMoO₄||CoMoO₄ supercapacitor in various voltage windows at a scan rate of 100 mV⁻¹ is shown in Fig. S3(a). It can be seen that the CoMoO₄ electrode has good electrochemical activity in a broad potential window in 1 M TEABF₄/PC electrolyte. For

a potential range of -1 to 1.5 V, the CV curve exhibits characteristic rectangular shape and indicates an ideal capacitive behaviour. As the potential increases to 2.5 V, the shape of the CV curve deviates from their rectangular shape due to the

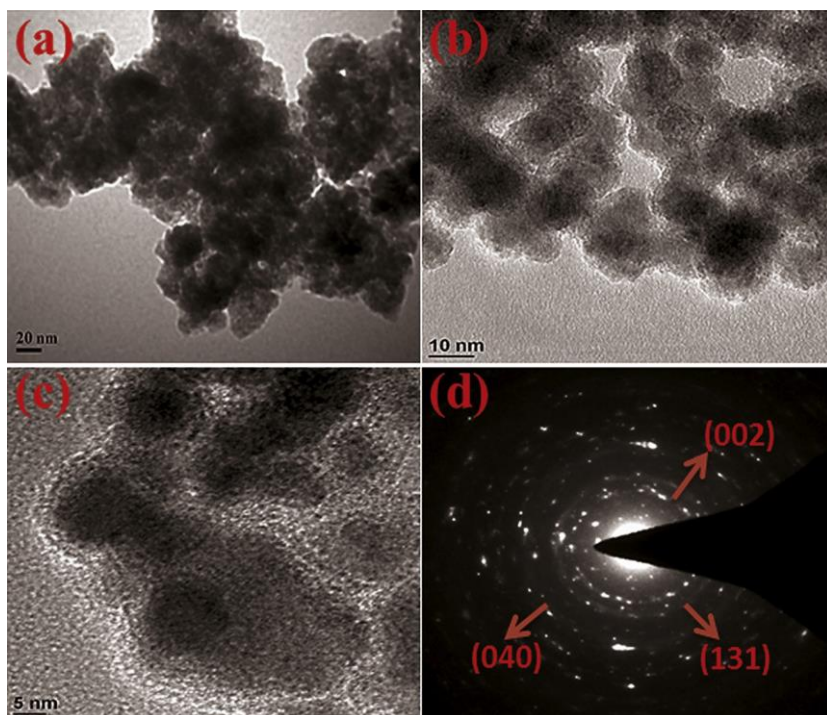


Fig. 3 (a-c) HRTEM images of CoMoO₄ nanoflakes, (d) the corresponding SAED pattern.

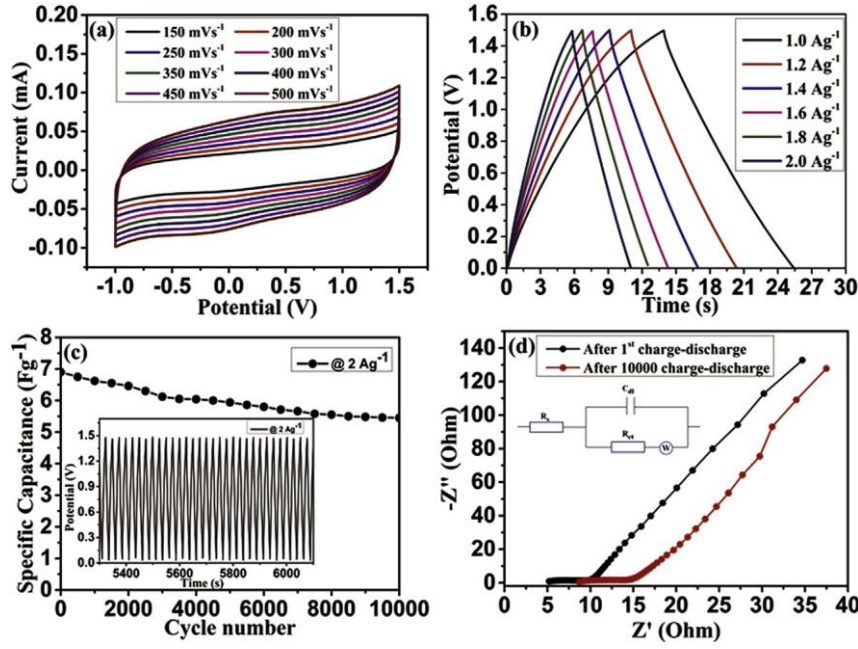


Fig. 4 (a) Cyclic voltammogram of CoMoO₄/CFC symmetric supercapacitor at various scan rates in 1 M TEABF₄/PC (b) Charge/discharge curves of symmetric supercapacitor at different current densities, (c) Cyclic stability at 2 A g⁻¹ over 10000 cycles (d) Nyquist plot of symmetric supercapacitor in 1 M TEABF₄/PC.

electrolyte decomposition. To date, the scan rate reported for metal oxide-based symmetric supercapacitors is limited to 200 mV s⁻¹ [35]. However, for practical applications this rate capability is not sufficiently high to provide higher energy and needs to be improved. In this study, we have measured the CV at different scan rates, ranging from 100 to 12,000 mV s⁻¹ and are depicted in Fig. 4(a) and Fig. S3(bed). From Fig. 4(a), it indicates that the supercapacitor maintained its rectangular shape and reversibility even at the high scan rate of 500 mV s⁻¹.

When the scan rate increased from 600 to 5000 mV s⁻¹, our symmetric supercapacitor retained the voltammetric shape and featureless current response at both anodic and cathodic sweeps as shown in Fig. S3(c and d), which demonstrate the ultra-fast rate capability of the device. At very high scan rates ranging from 6000 to 12000 mV s⁻¹, the device responds with rectangular CV features with slight deviation at the end potentials. This result further confirms the high-rate performance of the device. The specific capacitances with respect to scan rates are shown in Fig. S4 and the values are presented in Table 1 of ESI. The galvanostatic charge-discharge profiles measured in positive potential at different current densities is shown in Fig. 4(b) and reveals nearly linear time-potential relation, which describes the capacitive characteristic of the material. The specific capacitance (C_s) of the electrode was determined using the following equation:

$$C_s = I\Delta t/m\Delta V \quad (3)$$

where, I is the charge/discharge current, t is discharge time, ΔV is the potential limit during discharge, and m is the mass of the active material. While calculating the specific capacitance for CoMoO₄/CFC, the contribution of CFC was subtracted from

the total C_s value. To convince us of the contribution of CFC on specific capacitance we have measured the CV and charge-discharge for pure CFC in two electrode configuration with the same electrolyte. Fig. S5(a and b) shows the CV and charge-discharge curves of pristine CFC based symmetric supercapacitor. The CV curve at different scan rates ranging from 20 to 1000 mV⁻¹ showed the capacitive characteristic of the CFC. However, the observed current response is 1000 times lower than the CoMoO₄/CFC based supercapacitor, which describes a negligible contribution by the CFC to the measured capacitance. Similarly, the charge-discharge profile also clearly evidences the ideal capacitive behaviour with insignificant discharge time (only few seconds) as shown in Fig. S5(b) and delivered the specific capacitance of ~1 mF cm⁻² @ 0.5 mA cm⁻². Therefore it can be concluded that the measured capacitance mainly arises from the CoMoO₄ nano-flakes and not from the CFC.

The specific capacitances for CoMoO₄/CFC based supercapacitor are found to be 8.3, 7.3, and 6.9 F g⁻¹ for the corresponding current densities of 1, 1.4 and 2 A g⁻¹, respectively. 83% of initial capacitance was retained when the current density was increased to ~2 A g⁻¹, which indicates the very good capacity retention of the supercapacitor. This result was further compared with 3 M KOH electrolyte. Typical CV and charge/discharge curves of the CoMoO₄/CFC based symmetric supercapacitor measured in 3 M KOH electrolyte are shown Fig. S6(a and b). From the CV curves, the pseudo-capacitive characteristic of the device over the scan rates ranging from 10 to 100 mV s⁻¹ can be observed. The charge-discharge profiles also are in concordance with the CV results. The measured specific capacitances in 3 M KOH electrolytes are found to be 25.2, 16.9 and 9.3 F g⁻¹ for a current density of 0.5,

1.5 and 2.5 A g⁻¹, respectively. The observed specific capacitance in organic electrolyte is comparatively lower than the metal molybdate based symmetric supercapacitors investigated in alkaline electrolytes [35]. This may be due to the limited number of larger size organic (~1.4 nm) electrolyte ion diffusion via the inhomogeneous electrode pores and lead to partial contribution of surface active sites to the redox process [49,50]. In order to increase the capacitance value further, investigation is required on this material with a different electrolyte system. To date, aqueous electrolytes (KOH, H₂SO₄, etc.) are widely used to investigate the electrochemical capacitive features of the porous electrodes due to their high ionic conductivity and smaller ionic (~0.5 nm) size. However, their narrow potential window (~1 V), electrolyte leakage, corrosive behaviour and lower energy and power density, limits their large scale practical applications. Therefore, it is important to investigate the pseudo-electrochemical performance of the metal oxide electrodes in organic electrolyte systems. In organic electrolytes, it is possible to further extend the potential window to ~2.5 V, thereby enhancing the energy and power densities of the supercapacitor devices. Also, negligible leakage and limited corrosion by the organic electrolyte over long term usage, further increase the life span of the supercapacitors. However, the average specific capacitance in organic electrolytes is still quite low as compared to inorganic electrolytes and needs to be improved.

The long term cyclic stability of the symmetric supercapacitor was tested by continuous charge-discharge measurement over 10,000 cycles at a constant current density of 2 A g⁻¹. Fig. 4(c) shows the cyclic performance of the CoMoO₄||CoMoO₄ supercapacitor in organic electrolyte. The response confirms that the device exhibits an excellent cyclic stability and delivered 78.9% of capacitance retention after 10,000 cycles. To further understand the electrochemical kinetics electrochemical impedance analysis was carried out before and after 10,000 charge-discharge cycles. A typical Nyquist plot is shown in Fig. 4(d) together with the corresponding equivalent circuit. According to the equivalent circuit, R_s , C_{dl} , R_{ct} and W are the solution resistance, double layer capacitance, charge transfer resistance and Warburg's diffusion elements, respectively [47,51]. The device displays a pure capacitive behavior at low frequency and significant charge transfer kinetics at high frequencies. The estimated charge transfer resistance is 5.95 Ω and it was slightly increased to 6.14 Ω after 10,000 charge-discharge cycles. This result further supports the good electrical conductivity of the materials and low contact resistance at the electrode/electrolyte interfaces. The power and energy performance of the device was calculated using the following relations:

$$E = CV^2/2 \quad (4)$$

$$P = E/t \quad (5)$$

where E is the energy density, C is the specific capacitance, V is the potential limit, P is power density and t is discharge time. The active mass based energy and power density relation for CoMoO₄||CoMoO₄ symmetric supercapacitor is shown Fig. 5. Our device delivered an energy density of 2.6 Wh kg⁻¹ with the

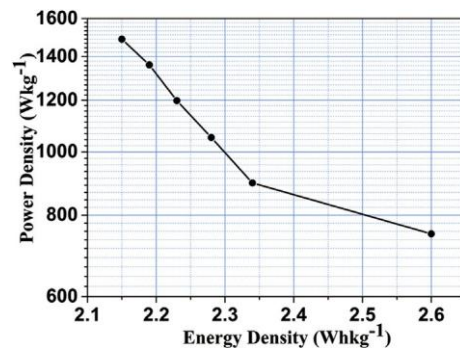


Fig. 5 Ragone plot of CoMoO₄/CFC based symmetric supercapacitor in 1 M TEABF₄.

power outcome of 748.8 W kg⁻¹ at a current density of 1 Ag⁻¹. When the current density was increased to 2 Ag⁻¹, the device exhibited 2.2 Wh kg⁻¹ of energy with 1488.5 W kg⁻¹ of power density. The observed energy and power performance of the organic electrolyte based symmetric supercapacitor is considerably higher than the symmetric supercapacitor measured in 3 M KOH. The inorganic device has delivered a specific energy density of only 2 Wh kg⁻¹ with a power density of 400 W kg⁻¹ at the same current density of 1 Ag⁻¹. Further increasing the current density to 2 A g⁻¹, the energy and power density decreased to 0.9 Wh kg⁻¹ and 800 W kg⁻¹, respectively. This increased energy and power performance of organic supercapacitor is mainly due to the increased potential window. However, only few reports are available where metal oxide based symmetric cell performance is investigated, particularly in the organic electrolytes [27,52]. In comparison to our earlier investigations, the present work with CoMoO₄/CFC electrode has delivered significant energy and power performance as comparable to the different metal oxide electrodes measured in inorganic electrolyte systems. Interestingly, the materials showed good capacitive behaviour in 1 M TEABF₄ with excellent rate capability up to 12000 mV s⁻¹ and reasonable specific capacitance. Also, our device exhibits superior cyclic stability with 78.9% capacity retention even after 10,000 cycles. These results show an improvement over devices from Veerasubramani et al., where they showed 84.7% retention after 4000 cycles at a current density of 1 mA cm⁻² in 1 M NaOH [53]. Our specific capacitance is significantly higher than the value reported for a hydrogenated ZnO core-shell nanocable based flexible supercapacitor (26 mF cm⁻² @ 0.5 mA cm⁻²) [54] and an Ru//Ru symmetric supercapacitor in 1 M Na₂SO₄ aqueous electrolyte, which showed only 67 mF cm⁻² @ 1 mA cm⁻² [55]. Also, this value is much higher than the symmetric capacitor based on Co₃O₄ nanowire/nanoflower/CFC hybrid structure in both 1 M TEABF₄ (4.8 mF cm⁻² @ 3 mA cm⁻²) and 3 M KOH (7.8 mF cm⁻²) electrolytes [27]. It should be noted that the energy and power performance of the CoMoO₄ based supercapacitor in organic electrolytes compares favourably with carbon-based symmetric devices [51]. Thereby, CoMoO₄ on CFC with a functional morphology and pore distribution is a potential electrode for supercapacitor application.

The electrocatalytic activity of CoMoO_4 nanoflakes towards methanol oxidation in alkaline medium was studied by cyclic voltammetry and chronoamperometry analysis. Typical catalytic response of CoMoO_4 catalyst in 1 M KOH þ 0.5 M CH_3OH is shown in Fig. 6(a-d). The CV curves in Fig. 6(a) indicate an excellent electrocatalytic activity of CoMoO_4 electrode by showing the well resolved redox peaks without methanol (Black) and effective methanol oxidation with high current density in the presence of methanol (Red). The electrode showed a peak current density of 25 mA cm^{-2} at 0.7 V. More importantly, our $\text{CoMoO}_4/\text{CFC}$ electrode exhibits a low onset potential of 0.38 V, lower than NiO (0.5 V), NiCo_2O_4 (0.42 V) and Co_3O_4 (0.56 V) catalysts grown on conducting substrates [43]. Thereby, it may be concluded that the $\text{CoMoO}_4/\text{CFC}$ has excellent electrocatalytic activity towards methanol oxidation. It can be noticed in Fig. 6(b) that increasing the scan rate from 5 to 50 mV s^{-1} resulted in the increase in oxidation current without any deviation in the redox peaks, even at the high scan rate of 50 mV s^{-1} . This result indicates the rapid electron/ion transfer kinetics in the electrode surface during methanol oxidation that is not limited by diffusion. The stability of the catalyst is one of the important factors for the usability of the electrode for longer time. Thereby, it was investigated with a chronoamperometric curve recorded for an extended time of 3000 s at an initial voltage of 0.38 V. As from Fig. 6(c), it can be seen that the electrode showed a sudden decay for a few seconds followed by stable current for 3000 s, which inferred the excellent electrochemical stability

of the catalyst. The catalyst showed a high current density even after 3000 s. This result confirmed that the CoMoO_4 nanoflake structure has a better tolerance towards the tenacious reaction intermediates such as CO and HCHO, which are usually formed during methanol oxidation to contribute to electrode poisoning [43].

Fig. 6(d) presents the Nyquist plots for $\text{CoMoO}_4/\text{CFC}$ recorded in 1 M KOH and 0.5 M CH_3OH in 1 M KOH. The measured impedance spectra showed a sloped line at low frequencies, relating to the diffusion process and semicircle at high frequency region due to electron transfer [56]. The observed incomplete semicircle infers the frequency limitation of the measurement. It is noticeable that the diameter of the semicircle is small, which is due to the superior electrical conductivity of the catalyst in 0.5 M CH_3OH . The observed impedance spectra were compared to the equivalent circuit as given in the inset of Fig. 6(d). From Fig. 6(d), the measured R_{ct} value is small ($\sim 3.72 \Omega$) for methanol electro-oxidation in 1 M KOH, indicating good tolerance of the catalyst against CO poisoning. Furthermore, it confirmed the effective contribution of $\text{Co}^{2+}/\text{Co}^{3+}$ for the methanol oxidation process, which resulted in a high catalytic current density. Thereby, it validated the usability of the CoMoO_4 nanoflakes on carbon fiber cloth as a potential electro-catalyst for methanol oxidation reaction.

The interesting bi-functional electrochemical features of hydrothermally grown CoMoO_4 nanoflake/CFC electrode were possibly due to their desired structural benefits. In brief, the highly flexible and conducting carbon fiber cloth substrate provided the good mechanical integrity and adhesion

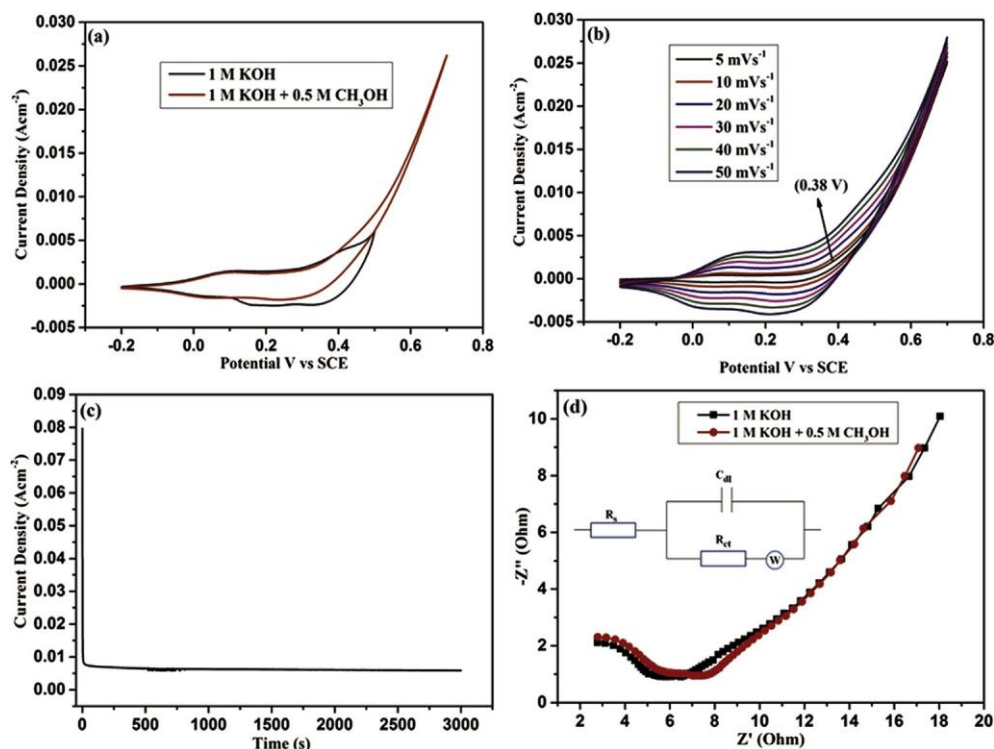


Fig. 6 (a) Cyclic voltammogram of $\text{CoMoO}_4/\text{CFC}$ measured in 1 M KOH and 1 M KOH þ 0.5 M CH_3OH at 20 mV s^{-1} (b) CV curves of methanol oxidation with various scan rates. (c) Amperometric curve of $\text{CoMoO}_4/\text{CFC}$ hybrid electrode and (d) Nyquist plot for CoMoO_4 catalyst with and without methanol.

between electroactive material and substrate area during faradaic reaction. Consequently, the nanoflakes have offered high exposed surface to electrolyte contact, which significantly enhanced the core-level redox process. The direct contact between metal oxide and CFC further supported the high electrical conductivity. Overall from this investigation it can be inferred that the growth of CoMoO₄ nanostructure on CFC can be used as a bi-functional electrode for both supercapacitor as well as direct methanol fuel cell applications.

Conclusions

In summary, porous CoMoO₄ nanoflakes consisting of ultra-fine nanocrystals were grown directly on the carbon fiber cloth by hydrothermal approach and were demonstrated to be superior bi-functional electrode material for energy storage and conversion devices. As a binder free electrode for symmetric supercapacitor, the CoMoO₄/CFC exhibited good electrochemical performance in 1 M TEABF₄ non-aqueous electrolyte with reasonable specific capacitance of 8.3 Fg⁻¹ at a constant current density of 1 Ag⁻¹. Furthermore, the capacitor showed reasonable energy and power performances and also showed good electrochemical reversibility for long term applications. Interestingly, the CoMoO₄/CFC showed methanol electro-oxidation with high current density (25 mA cm⁻²) at lowest onset potential (0.38 V) as an anode material for DMFC. This bi-functional electrochemical activity of the electrode is mainly due to the advantages through their desired 3D hierarchical porous nanoflake microstructure, good electrical conductivity, and integration of CoMoO₄ with CFC.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.ijhydene.2015.09.127>.

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